Nature of H_2 Adsorption Sites in
Cu/ZnO Synthesis Catalysts

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Abstract

For a co-precipitated Cu/ZnO mixture that is representative of methanol
synthesis catalysts, we observe that H_2 adsorption occurs at isolated Cu
sites on the catalyst surface. These H_2 adsorption sites differ from
those previously observed on pure ZnO samples in two respects: The range
of H_2 desorption energies is significantly higher (21-30 kcal/mole for the
10:90 Cu:ZnO mixture, vs. 16-21 kcal/mole for pure ZnO), and the pretreat-
ment temperature needed to activate the sites is lower (523 K for the
Cu/ZnO mixture, vs. 673 K for pure ZnO). This suggests that the enhanced
activity of Cu/ZnO catalysts, relative to ZnO catalysts, is due to Cu
sites that adsorb H_2 more strongly and which maintain their activity at
lower temperatures.

Introduction

Catalysts for the direct synthesis of alcohols from $CO:H_2$ mixtures must
satisfy two functional requirements. They must activate the CO molecule for re-
duction without directly dissociating the C-O bond, and they must activate the
H_2 molecule to perform the reduction. These two functions are combined quite
effectively in the Cu/ZnO catalysts for methanol synthesis (1,2), which hydro-
genate CO to CH_3OH with better than 99% selectivity (3).

Understanding the hydrogenation mechanism on these ZnO-based catalysts is
important, not only for selecting the optimum operating conditions for methanol
catalysts but also for designing catalysts to perform higher alcohol synthesis or
other hydrogenation reactions. As a prerequisite for understanding the hydrogen-
ation mechanism itself, in this paper we discuss our current knowledge of the H_2
adsorption sites on ZnO and Cu/ZnO mixtures.

H_2 Adsorption on ZnO

The distinguishing feature of H_2 adsorption on oxide catalysts is that
adsorption occurs <u>via</u> heterolytic dissociation of the H_2 molecule at polar
surface sites consisting of co-ordinatively unsaturated cation-anion pairs.
On ZnO, this adsorption process has been conclusively shown to occur at so-called
Type I sites (4-7):

$$H_2 + {}^{..}_{-Zn} - \overset{..}{O}- \rightleftharpoons \overset{H}{-Zn} - \overset{OH}{O}- \qquad 1)$$
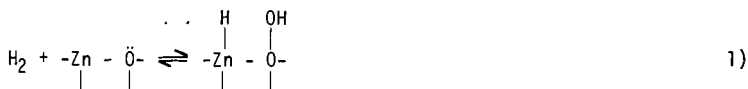
Reaction 1 is demonstrated by bands in the IR spectrum of H_2-saturated catalysts at 1710 cm-1 and 3490 cm-1, assigned to Zn-H and O-H stretching vibrations respectively (4-7).

The energetics of the Type I adsorption sites are fairly complex. Adsorption is activated but reversible at room temperature. A range of adsorption and desorption energies are observed, suggesting that more than one kind of Type I site exists. The equilibrium adsorption energy is 12-13 kcal/mole, the activation barrier for adsorption is 3-8 kcal/mole, and the desorption energy is 16-21 kcal/mole (7).

A second type of H_2 adsorption state has also been identified that is irreversible at room temperature (5). This so-called Type II state is not IR active, and consequently has not been studied as intensively as the Type I state. Dent et al. (8) have shown that Type II hydrogen is not involved in hydrogenation reactions, at least for the case of ethylene hydrogenation. The authors go on to speculate that Type II hydrogen may be bound in sub-surface sites, and therefore is non-reactive. While this remains to be proven conclusively, we will restrict the remaining discussion to Type I sites.

The geometry of the Type I sites has been partially determined. Temperature programmed desorption experiments show that H_2 molecules are adsorbed at spatially discrete sites: The coverage dependence of the TPD spectra indicate that desorption obeys first-order kinetics (cf. Fig. 1 below). Also, co-adsorbed H_2-D_2 mixtures retain most of their isotopic identity when desorbed. Both results are in marked contrast to the second order desorption kinetics and isotopic scrambling seen in TPD spectra of H_2 and D_2 on metals, where H atoms may interact with any of several neighbors during desorption.

The Type I sites are located within next-nearest neighbor proximity of each other. This is shown by the shifts of the ZnH and OH vibrational frequencies that occur as H_2 coverage increases. These shifts can be explained on the basis of electrodynamic and inductive interactions between oscillating ZnH and OH dipoles, provided that H_2 molecules adsorbed at different sites are within two lattice spacings of each other (9). (The shifts do not appear to be caused by long range electronic interactions involving the ZnO conduction band electrons, because the background transmission of the sample, and hence the Fermi level, remains unchanged during H_2 adsorption). Further evidence that the sites are spatially proximate is given by the observation that scrambling of H_2-D_2 mixtures does occur readily over ZnO at room temperature, where adsorption is reversible (5). This shows that migration and exchange between Type I sites does occur, albeit with a modest activation barrier.

Additional information about the nearest-neighbor geometry of the sites is provided by spectroscopic measurements of co-adsorbed $CO:H_2$ mixtures (10,11). These results show that the ZnH vibrational band undergoes two sequential, discrete frequency shifts as the CO coverage is increased. In contrast, the OH vibration shows only a continuous frequency shift with increasing CO coverage. Thus the Zn cation of the Type I sites appears to have two nearest neighbor sites that can adsorb CO, while the O anion of the Type I site has no such neighbors. Since the CO adsorption state that is occupied under the conditions of these experiments is known to occur at co-ordinately unsaturated Zn cations (12), this leads to the perhaps surprising conclusion that the Zn cation of the Type I site has two unsaturated Zn cations as neighbors, while the O anion has no unsaturated cations as neighbors (other

than its own Type I cation partner). However, such a "triad" of unsaturated Zn cations would be expected at an $O^=$ vacancy produced when a three-fold co-ordinated surface O anion is removed from the surface layer (10). Moreover, if this anion vacancy is produced by a dehydration reaction with the proton of a neighboring surface OH group, then the unsaturated O anion that remains after proton removal can serve as the anion partner in the Type I site.

Such oxygen vacancies can be most easily imaged on the basal (0001) oxygen plane (10). This is supported by the fact that Type I sites are most easily observed on powdered samples that contain a large fraction of polar planes in their crystal morphology (13), and also by the fact that sublimation occurs more readily on the basal oxygen face (14). However, recent studies of ZnO single crystal surfaces have raised the possibility that such vacancies might also be produced at step defects on the (10$\bar{1}$0) prism planes (15,16).

One other important feature of the Type I sites is their strong poisoning by adsorbed H_2O or CH_3OH (5):

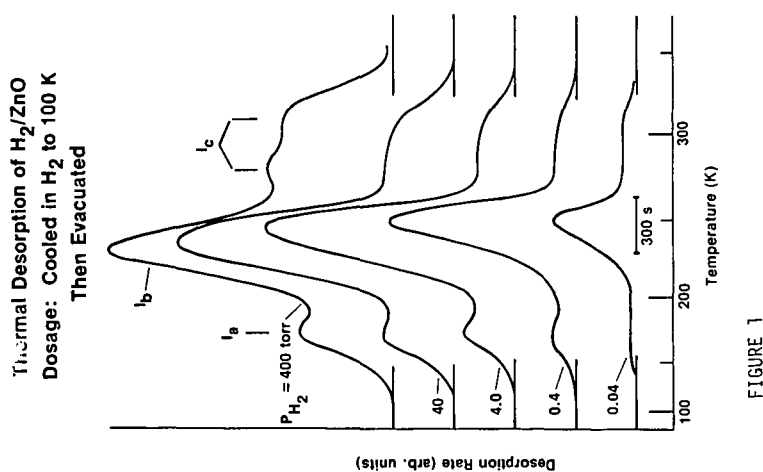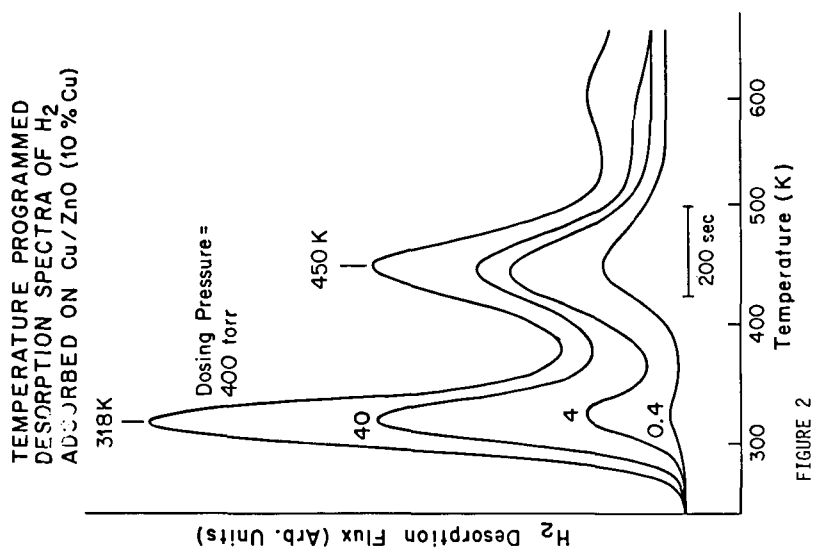$$ROH + -Zn - O- \rightleftharpoons \overset{OR}{\underset{|}{Zn}} - \overset{H}{\underset{|}{O}}- \qquad 2)$$

Reaction 2 is irreversible at room temperature, indicating that the desorption energy of these adsorbates is much greater than for H_2. Quantitative measurements of the desorption energies are still needed.

It is generally believed that the activation mechanism for producing the Type I site is dehydration to produce a cation-anion pair site. While this is certainly a necessary condition, experience in our laboratory has shown that it is not sufficient. Heating ZnO samples to less than 673K produces highly dehydrated surfaces, as indicated both by a sharp decrease in the IR bands due to residual OH species on the sample, and by the ability of the sample to re-adsorb H_2O. However, these surfaces are not active for the adsorption of H_2. In light of the discussion above, this suggests that an additional requirement for activating the Type I sites is that the dehydration step must also produce an $O^=$ anion vacancy. Adsorption of H_2O or CH_3OH thus represents a strong poisoning reaction, because these species re-occupy the $O^=$ vacancy.

H_2 Adsorption on Cu/ZnO

The results discussed above have been obtained for pure ZnO. While the ZnO Type I sites have been suggested as the source of the hydrogenation activity in Cu/ZnO synthesis catalysts (3), their presence has not been conclusively demonstrated on Cu/ZnO mixtures. As a first test for their presence, we therefore examined the H_2 adsorption behavior of a Cu/ZnO mixture with a 10:90 Cu:Zn ratio, prepared using the co-precipitation technique described by Hermann et al. (3).

In figures 1 and 2 we compare the H_2 desorption spectra of pure ZnO and the Cu/ZnO mixture. After outgassing each sample at the necessary temperature, the spectra were obtained by admitting the indicated pressure

TEMPERATURE PROGRAMMED
DESORPTION SPECTRA OF H_2
ADSORBED ON Cu/ZnO (10 % Cu)

Dosing Pressure =
400 torr

318K

450 K

40

4

0.4

200 sec

Temperature (K)

H_2 Desorption Flux (Arb. Units)

FIGURE 2

Thermal Desorption of H_2/ZnO
Dosage: Cooled in H_2 to 100 K
Then Evacuated

I_c

I_b

I_a

P_{H_2} = 400 torr

40

4.0

0.4

0.04

300 s

Temperature (K)

Desorption Rate (arb. units)

FIGURE 1

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of H_2 to the sample cell at room temperature, cooling the sample to 100K, evacuating the non-adsorbed gas, and then warming the sample (heating rate = 1.5 K/sec) while monitoring the flux of desorbing H_2. This dosing procedure was required to overcome the activation barrier for adsorption noted above.

The results for pure ZnO (Figure 1) have been discussed elsewhere in more detail (7). First we note that the spectra are quite complex, suggesting the presence of multiple binding states. The amount of H_2 adsorbed increases with dosing pressure, indicating that the activation barrier for adsorption increases with coverage. The peak temperatures are only weakly dependent on coverage, indicating first order kinetics. (First order kinetics are also indicated by the absence of isotopic scrambling, as noted above). The peak temperatures occur at 170, 240, 270, and 310 K, corresponding to desorption energies of 12, 16, 18, and 21 kcal/mole, respectively. No additional information about the individual states corresponding to each peak is available, except that the state at 170 K has a unique OH vibrational frequency and a small enough desorption energy that it is not occupied at room temperature. Finally, we note that it is necessary to outgas the sample at 673 K or above in order to observe any of these H_2 adsorption states.

The spectra for the Cu/ZnO samples are shown in Fig. 2. As was the case with pure ZnO, we see that the amount adsorbed increases with dosing pressure, indicating that adsorption is an activated process and that the activation barrier increases with coverage. The peak temperatures are again independent of H_2 coverage, suggesting first order desorption kinetics. However, two differences from the results for ZnO are observed: The peak temperatures are 310 K and 450 K, corresponding to desorption energies of 21 and 30 kcal/mole. These are higher than the range of energies found for ZnO. In addition, these experiments were performed using samples outgassed at 523 K, instead of the 673 K needed for ZnO. As mentioned above, pretreating ZnO at the lower temperature results in a surface with negligible H_2 adsorption capacity.

Discussion

We first consider what these results indicate about chemical bonding at the adsorption sites on Cu/ZnO catalysts. The fact that H_2 adsorption is observed after pretreatment at much lower temperature for the Cu/ZnO mixture than for pure ZnO indicates either that Cu species make it easier for the Type I ZnO sites to be activated, or else that Cu species themselves can function as the cations in Type I sites that have a much lower activation temperature. Competitive adsorption experiments with $CO:H_2$ mixtures described elsewhere (17) indicate that the latter explanation is correct; that is, the Cu species themselves participate as the cations in Type I sites analogous to those found on pure ZnO. The lower temperature required to activate the Cu sites suggests that the $O^=$ vacancy needed at a Type I site is more easily produced at a Cu neighbor, which is consistent with the lower enthalpy of decomposition of bulk CuO (36 kcal/mole for CuO, vs. 81 kcal/mole for ZnO (18)).

The higher desorption energy for H_2 may be the result of the d-electron vacancy on a divalent Cu cation, which would stabilize the CuH hydride bond (19).

Finally, we consider the implication of these results for the hydrogenation

mechanism on Cu/ZnO catalysts. The lower pretreatment temperature needed to activate the Cu Type I sites is remarkably consistent with the lower operating temperature required for Cu/ZnO synthesis catalysts, relative to the high pressure ZnO catalysts. The stronger H_2 adsorption energy may also contribute to the improved activity of the Cu/ZnO catalysts, although more detailed knowledge of the energetics of the subsequent reaction steps is needed before this conclusion can be stated with certainty. Finally, it is interesting to note that this H_2 adsorption behavior has not been reported for Cu species prepared on other supports. This suggests that the basicity and/or the tetrahedral coordination geometry of the ZnO lattice may be necessary to generate Type I cation-anion sites. This last point suggests that the potential of ZnO as a support material for hydrogenation catalysts should be more fully explored.

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